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UPGRADE OF PRODUCTION TECHNOLOGY OF BUILDING CERAMICS AND EXPANSION OF PRODUCT RANGE

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It is established that a marl additive to clays from Tatarstan deposits makes it possible to substantially expand the color range of ceramic products and to improve their physicochemical parameters. The methods of studies performed are described in detail.

The expansion of construction in the Republic of Tatarstan and the renaissance of the age-long practice of building brick houses calls for increased production of ceramic brick, which is an environmentally safe and durable material. The EU countries extensively use brick in housing construction. In the Republic of Tatarstan the constraining factor is the lack of advanced technologies and machinery for producing a wide range of building ceramic materials with adequate strength and decorative properties. As the result, the republic imports around 120 million conventional bricks per year while the local production is 224.8 million bricks. This increases the cost of construction due to substantial transportation expenses and is economically unacceptable for the local producers. Therefore, the target of the manufacturers of ceramic brick in the Republic of Tatarstan is not only to upgrade the brick quality, but also to expand the range of products made from local materials.

The brick factories in Tatarstan currently use local argillaceous materials represented by low-melting polymineral clays, frequently with a high content of carbonates. As a rule, this material is no good for bricks better than grade M125.

The strength parameters of brick can be improved either by introducing expensive additives, or by using effective clay combinations. An optimum selection of compositions can yield products of adequate quality.

The introduction of expensive additives is not cost-effective and leads to a substantial price increase, which makes the product noncompetitive. Therefore, the Stroitel'naya Keramika Research and Production Company has chosen another approach to improving the quality of product: the development of ceramic mixtures with optimum mineralogical compositions ensuring products with preset qualities.

Red-burning and light-burning clay deposits have been discovered in the Republic of Tatarstan [1]. Their application will make it possible to significantly increase the range of ceramic items and to start the production of ceramic brick of a grade superior to grade M125 with a wider color range.

One of the main factors currently preventing realization of the potential of local materials is insufficient scientific understanding and prediction of physicochemical processes in firing. The experience of Western companies, including Italians ones, in the production of construction ceramics [2] shows that without researching polymineral materials (including mineral additives) and physicochemical processes occurring in clay and mixtures under firing it is impossible to organize a state-of-the-art production facility.

It is known that optimal compositions of material mixtures can be based on the traditional analysis of the granulometric composition of argillaceous materials using the Winkler diagram or the Chumachenko – Chudin contemporary program complex for estimating the mineral composition of materials. Based on the chemical composition, we can determine the amount and composition of melt in ceramic articles and these data are used to predict their density and strength.

Phase diagrams of ternary aluminosilicate systems are used to determine the content of melt in a material at the corresponding firing temperature. Knowing the chemical composition of the batch and the compositions of low-melting eutectics, one can calculate the quantity and composition of melt for any temperature.

However, practice shows that the chemical composition cannot always provide exhaustive information. By way of illustration, Table 1 gives a comparative analysis of the chemical composition of clay and a variety of granite [3]. Considering the similarity in the chemical composition of the two rocks, one could expect the quantity and composition of melt to coincide at certain firing temperatures, which contradicts experimental data. The essential factor is a significant difference in the mineral composition of the specified rocks.

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TABLE 1

Material	Weight content, %								
	SiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O
Clay	58.1	15.4	4.0	2.5	–	2.4	3.1	1.3	3.2
Granite	69.1	14.5	1.7	2.2	0.1	1.1	2.6	3.9	3.8

Consequently, it is impossible to improve production technologies for building ceramics without taking into account the mineral composition of raw materials and the products of their firing.

Thus, the use of the above methods in our case was insufficiently informative and did not give a positive result. Therefore, our main efforts were directed to identifying and studying the phase composition of argillaceous polymineral material with additives of calcareous clay (marl) and the products of firing of their mixtures.

It is known that the composition and the quantitative ratio of newly formed phases have a significant effect on the formation of structure of ceramic products in firing [4, 5]. It is believed that by developing respective compositions of argillaceous materials taking into account their chemicomineralogical composition one can control the processes of phase formation. Therefore, it is interesting to study the processes of firing polymineral materials, the mechanism of additives, and the effect of the firing atmosphere on structure formation in ceramic mixtures and their physicomechanical properties.

The authors in [6] noted the effect of strength increase in facing brick when crushed chalk was added into mixtures. However, using chalk has the disadvantages of the deterioration of the plastic and molding properties of the batch and the need for additional labor-consuming operations of milling chalk and mixing it with clay mixtures, which increases the production cost.

Light-colored brick can be produced by using any carbonate-bearing additive. Such additive in our case was calcareous marl from the Maksimkovskoe deposit located in the Tetyushskii District of the Republic of Tatarstan. The main material was brick clay from the Koshchakovskoe deposit situated near Kazan.

The positive property of marl is its higher plasticity than that of standard brick clay (Table 2), which improves the plastic and molding properties of the batch constituting a mixture of two types of materials.

Another positive property of marl is the high content of calcite: around 44% (Table 3).

According to the data of x-ray phase analysis, the composition of Maksimkovskoe marl differs from Koshchakovskoe clay only by its lower content of argillaceous minerals and quartz and its higher content of calcite.

Electron microscope analysis indicates that marl calcite is uniformly distributed in the marl rock, is a disperse phase of organogenic origin, and is formed by algae (Fig. 1).

Koshchakovskoe clay by its degree of plasticity belongs to the moderately plastic group. An additive of 30% Maksimkovskoe marl raises its plasticity number from 7.5 to 16.4 and such clay mixture becomes medium plastic, which improves the molding properties of the batch.

To test clays from the specified deposits, their mixtures with marl additives were molded as bars of size $160 \times 40 \times 40$ mm. The dried material was crushed in a DGSh 160×100 jaw crusher to a particle size below 2 mm, after which experimental mixtures were prepared adding 10, 20, 30, 40, and 50% Maksimkovskoe marl. The resulting batch was twice treated in the laboratory mixing screw and once with laboratory rolls. The batch was mixed with water up to the molding moisture and held for 24 h. The prepared mixtures were used to mold samples. The mixtures had satisfactory molding capacity.

The samples were dried on shelves in a room, then in the drying cabinet at a temperature of 35 – 80°C. Firing was performed at a temperature of 980°C in a SNOL-1,6,2,5, 1/9-PZ electric furnace. The firing conditions were as follows: temperature rise up to 500°C — 8 h, exposure at 500°C — 3 h, from 500 to 700°C — 4 h, from 700 to 850°C — 6 h, from 850 to 980°C — 2 h, exposure at the final temperature — 2 h, cooling to 50 – 60°C — 24 h.

The effect of the marl content on the physicomechanical properties of samples molded by the ramming method (firing temperature 980°C) is shown in Table 4.

Marl added to polymineral clay from the Koshchakovskoe deposit increases the strength parameters of pro-

TABLE 2

Clay	Plasticity limits		Plasticity number	Classification of argillaceous material based on plasticity number
	lower bound of fluidity	rolling boundary		
Koshchakovskoe	26.3	18.8	7.5	Moderately plastic
Maksimkovskoe	47.1	26.6	20.5	Medium plasticity

TABLE 3

Clay	Weight content, %												
	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	FeO	MnO	CaO	MgO	Na_2O	K_2O	P_2O_5	SO_3 (total)	calcination loss	quartz
Koshchakovskoe	73.53	10.84	–	3.50	2.30	–	2.54	1.60	2.80	1.20	–	–	4.31	–
Maksimkovskoe	33.24	11.36	0.58	3.17	0.41	0.04	24.57	1.52	0.23	2.03	0.06	0.28	22.82	8.32

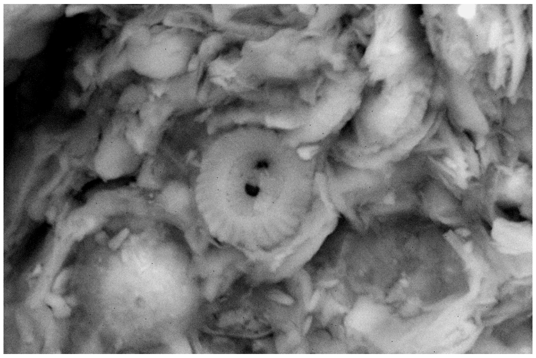

Fig. 1. Electron microscope photo of marl from Maksimkovskoe deposit (organogenic alga calcite shaped as “buttons”).

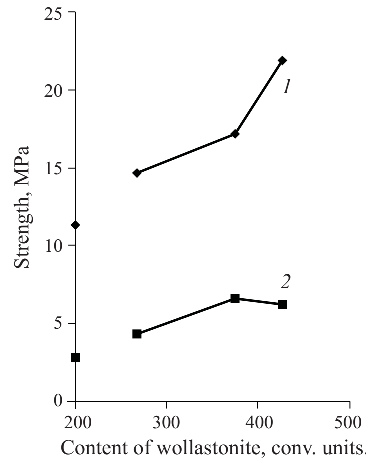

Fig. 2. Dependence of compressive (*1*) and bending (*2*) strength of ceramic samples on their content of wollastonite.

ducts after firing. At a firing temperature of 980°C the compressive strength, depending on the additive content, grows by 30 – 90%, and the bending strength grows 1.5 – 2.4 times. The presence of marl in the batch slightly increases the water absorption of samples. There is no perceptible effect on shrinkage. A positive property of marl additive is decreasing the drying sensitivity of the batch. It is established that the optimum quantity of Maksimkovskoe marl introduced in Koshchakovskoe clay is 30 – 40%. The marl additive also allows for modifying the color range of ceramics (from pink to light yellow) and improves the strength parameters of products, i.e., improves the grade of the brick.

The increased strength of ceramics is accounted for by data of x-ray phase analysis used to identify the phase composition of materials and products of firing. The mineral composition of samples is as follows:

– relic minerals: quartz, feldspars;

– newly formed minerals: hematite Fe_2O_3, wollastonite $CaSiO_3$, melilite $(Ca, Na)_2(Al, Mg, Fe)[(Si, Al)_2O_7]$, pyroxene close to hedenbergite of composition $CaFe[Si_2O_6]$, and the amorphous (presumably alumosilicate) phase.

Analysis of the obtained diffraction patterns of ceramic bars revealed their significantly different composition of emerging crystalline phases.

The only new crystalline phase registered in the sample of Koshchakovskoe clay fired at 980°C is hematite, whereas samples with 30% marl additive (fired at the same temperature) contain such newly formed crystalline phases as wollastonite, melilite, and pyroxene, while hematite is not identified. All samples contain an amorphous component as well. None of the samples with marl additive exhibited products of thermal dissociation of calcite, which is contained in initial material, nor the product of lime hydration, i.e., portlandite $Ca(OH)_2$.

An obvious correlation is observed between the mineral composition of ceramic samples and their color shades and physicomechanical properties:

– hematite impurity responsible for the red color in fired samples is registered in the diffraction patterns of samples containing not less than 20% marl;

– there is a direct correlation between the content of newly formed wollastonite and the strength of material.

The absence of hematite in ceramic samples in which the marl content constitutes over 20% can be attributed to the incorporation of iron in the melilite and pyroxene structure, which is facilitated by the presence of CaO (the product of thermal dissociation of calcite). Hence the transformation of red-brown tint into yellow shades in ceramic samples with the marl additive is due to a decreased content of hematite. The increased strength of samples made of the batch containing marl combined with Koshchakovskoe clay can be attributed as well to the presence of newly formed wollastonite, which is absent from fired samples of traditional brick clays. A certain dependence is observed: with increasing marl additive in the batch and, accordingly, the growing content of wollastonite in ceramic samples, their strength grows (Fig. 2).

Similar results were obtained analyzing mixtures of clays from other deposits of the Republic of Tatarstan (Nizhne-Suksinskoe, Alekseevskoe) with marl from the Maksimkovskoe deposit.

At the same time, certain regularities of the behavior of samples depending on the firing atmosphere have been es-

TABLE 4

Parameter	Sample with marl additive, wt.%			
	without additive	20	30	40
Strength, MPa:				
compressive	11.3	14.7	17.2	21.9
bending	2.8	4.3	6.6	6.2
Water absorption, %	12.2	13.8	15.0	15.1
Shrinkage, %:				
air	6.3	8.0	7.4	8.0
total	6.4	8.3	7.8	8.7
Molding moisture, %	18.4	21.2	19.8	20.8
Drying sensitivity coefficient, sec	104	113	127	166

tablished. Thus, the strength of brick made from the same batch composition, which is a mixture of Aleskeevskoe clay (45%), Maksimkovskoe marl (45%), and river quartz sand (10%), is higher when the brick is fired in an industrial furnace having a more reducing atmosphere. In the same conditions lighter-colored brick was produced. It should be noted that so far it is not possible to precisely estimate the redox potential of the gaseous firing medium in industrial conditions. However, a certain correlation between the content of wollastonite and the firing atmosphere is observed.

The content of wollastonite is higher in samples fired in a more reducing atmosphere due to the lower content of pyroxene, and the degree of crystallization of wollastonite and melilite is higher as well.

Evidently, the increased content of wollastonite in the considered ceramic articles is caused by adding marl that contains calcite as one of the main minerals. The mechanism of calcite in a fired batch consists in its thermal dissociation [7] and reaction of lime (calcium oxide) with the products of thermal destruction of argillaceous minerals with the formation of wollastonite which is responsible for the strength of the material obtained.

Thus, a marl additive to the specified clays makes it possible not only to expand the color range of materials but also to improve their physicomechanical characteristics. In this context one can consider expanding the ceramic product range at existing brick factories, including the Stroitel'naya Keramika Production Company using local materials.

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